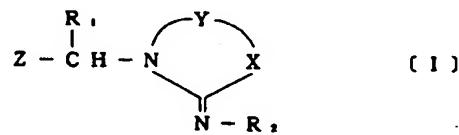




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containing the same: wherein Z represents a 5- or 6-membered nitrogenous hetero-cyclic group which may be substituted; X represents carbon, nitrogen, sulfur or oxygen; Y represents  $-CR_3 = CR_4 - CR_5 R-$ , etc.; R<sub>2</sub> represents an electron drawing group except for nitro, cyano and trifluoroacetyl; R<sub>1</sub> and R<sub>3</sub> to R<sub>5</sub> represent each hydrogen, halogen or lower alkyl which may be substituted.



Field of the Invention

The present invention relates to novel heterocyclic compounds, a process for the preparation thereof and a insecticide.

5

Background Art

By virtue of research and development of insecticides for many years, a number of insecticides, for example organophosphorus insecticides such as parathion and malathion, and carbamate insecticides such 10 as carbaryl and methomyl, have been developed and used in practice. The contribution these insecticides to the improvement of agricultural production yield are great.

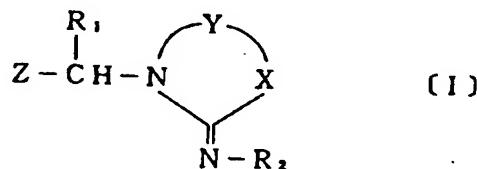
However, in recent years some of these insecticides have had their use regulated because of problems such as environmental pollution due to residue or accumulation, or because they cause infestation of 15 resistant insect pests as a result of long-term use. Therefore, the development of novel insecticidal compounds which have excellent insecticidal property against insecticide-resistant pest insect species as well as other various pest insects and can be safely used is highly demanded.

As cross references, Japanese Patent Application Laid-Open No.Sho 63-150275, No.Hei 3-190859 which disclosed the compounds having similar structural formula to the heterocyclic compounds of this invention have been known.

20 It is an object of the present invention to provide an agricultural chemical which can be manufactured advantageously on an industrial scale and can be used safely as well as having firm insecticidal effectiveness.

The present invention is directed at compounds having the general formula [I]:

25

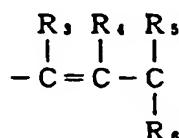


30

wherein

35 Z is an unsubstituted or substituted 5- or 6-membered heterocyclic group containing nitrogen;  
X is a carbon, nitrogen, sulfur or oxygen atom;  
Y is, when X is a carbon atom, (a) in a form of -Y-X;  
(a)

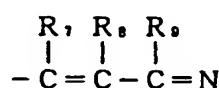
40



45

when X is a nitrogen atom, (b) or (c) in a form of -Y-X;  
(b)

50



55

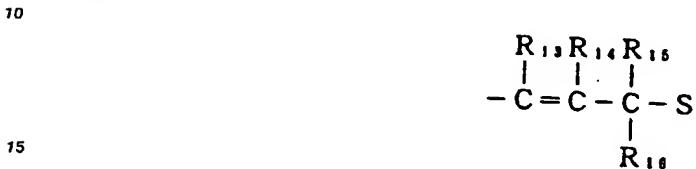
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(c)



when X is a sulfur atom, (d), (e) or (f) in a form of -Y-X;

(d)



(e)



25 (f)



when X is an oxygen atom, (g) or (h) in a form of -Y-X;

(g)



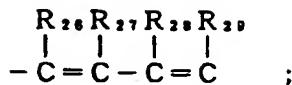
(h)



50 R<sub>2</sub> is an electron attractive group other than nitro, cyano and trifluoroacetyl;  
 R<sub>1</sub> and R<sub>3</sub> ~ R<sub>25</sub> are independently a hydrogen atom, a halogen atom or an unsubstituted or substituted lower alkyl;  
 Or, Y is, when X is a carbon atom, (i) in a form of -Y-X;

55

(i)



R<sub>2</sub> is an unsubstituted or substituted heterocycle carbonyl, other than furancarbonyl, thiophenecarbonyl and pyridinecarbonyl;

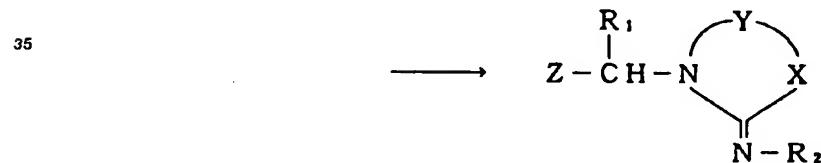
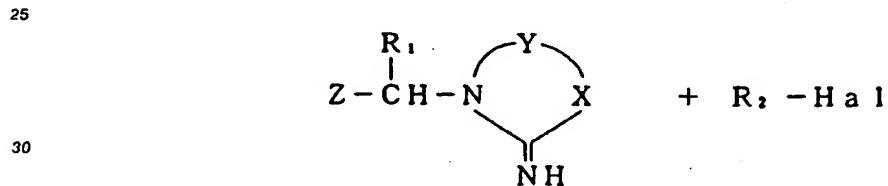
10 R<sub>26</sub> ~ R<sub>29</sub> are independently a hydrogen atom, a halogen atom or an unsubstituted or substituted lower alkyl;

and a process for the preparation of the compounds and an insecticide.

15 Electron attractive groups represented by R<sub>2</sub> are for example alkoxy carbonyl including C<sub>1</sub>-4 alkoxy carbonyl such as methoxycarbonyl and ethoxycarbonyl; C<sub>6</sub>-10 aryl carbonyl such as phenyl carbonyl; heterocyclic carbonyl such as pyridinecarbonyl, thiophenecarbonyl and pyrazinecarbonyl; C<sub>1</sub>-4 alkylsulfonyl which can be substituted by halogen such as chlorine and bromine, for example, methylsulfonyl, trifluoromethylsulfonyl and ethylsulfonyl; sulfamoyl; C<sub>1</sub>-4 acyl which can be substituted by halogen such as chlorine and bromine, for example, acetyl and trichloroacetyl, and carbamoyl.

20 Best Mode for Carrying Out the Invention

The process for preparing the compounds specified in the present invention is as follows.



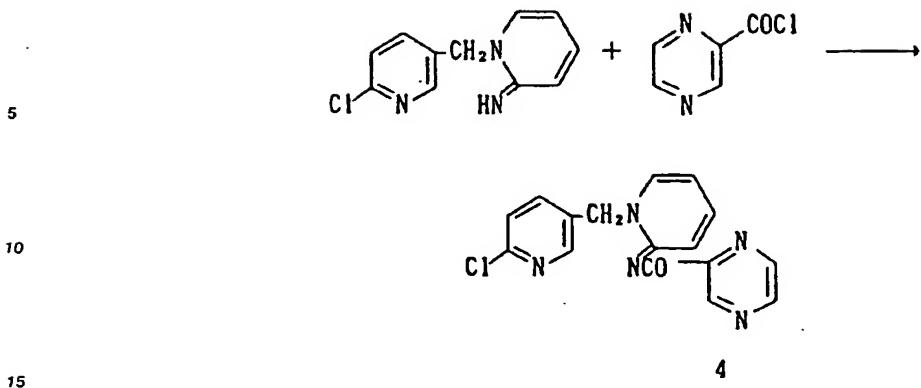
wherein Hal is a halogen atom, Z, X, Y, R<sub>1</sub> and R<sub>2</sub> are as defined above. Triethylamine, NaH, Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> etc. are used as an acid acceptor in an inactive solvent such as acetonitrile, methylethylketone, acetone, DMF and the like. The product, in general, can be synthesized by heating at a temperature in the range from room temperature to the boiling point of the solvent used.

45 The structures of the compounds specified in the present invention were determined based on the analytical results obtained by utilizing IR, NMR, MS and other analytical means.

The compounds specified in the present invention are illustrated in detail by the following Examples.

50 Example 1

1-(2-chloro-5-pyridylmethyl)-2-(pyrazinecarbonylimino)-1,2-dihydropyridine (Compound No. 1):

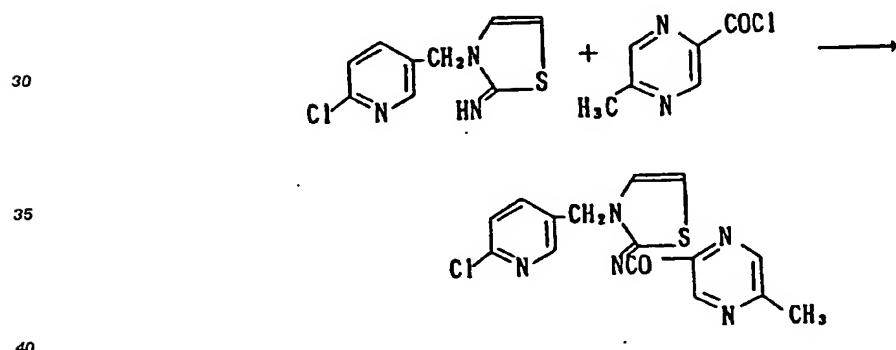


1.2 g of pyrazinecarbonyl chloride, and 1.4 g of triethylamine were added to a solution of 1.5 g of 1-(2-chloro-5-pyridylmethyl)-2-imino-1,2-dihydropyridine in 30 ml of acetonitrile.

After refluxing for 3 hours, acetonitrile was distilled off, and the residue was purified by column chromatography to give 1.4 g of the intended product.

### Example 2

3-(2-chloro-5-pyridylmethyl)-2-(5-methyl-2-pyrazinecarbonyl-imino)-2,3-dihydrothiazole (Compound No. 152);



1.1 g of 5-methyl-2-pyrazinecarbonyl chloride, and 0.9 g of triethylamine were added to a solution of 1.5 g of 3-(2-chloro-5-pyridylmethyl)-2-imino-3,3-dihydrothiazole in 30 ml of acetonitrile.

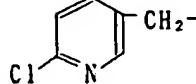
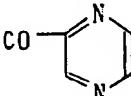
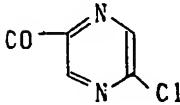
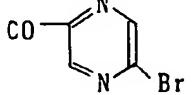
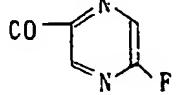
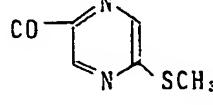
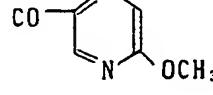
After refluxing for 3 hours, acetonitrile was distilled off, and the residue was purified by column chromatography to give 1.6 g of the intended product, m.p. 205-206°C.

The compounds of the present invention are illustrated in Table 1 including the Examples described above.

50

55

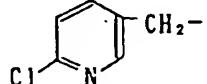
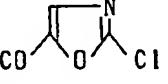
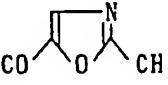
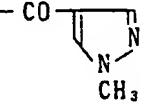
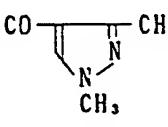
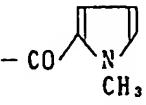
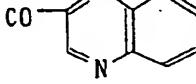
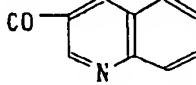
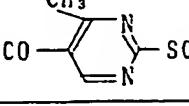
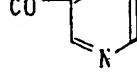
Table 1

Compound No.	Structure Formula			Physical Properties ( ) m.p. °C
	$Z - \overset{R_1}{\underset{ }{C}} H - N$	$\text{Y} \curvearrowright$	$\text{N} = R_2$	
	$Z - \overset{R_1}{\underset{ }{C}} H$	$- Y - X$	$R_2$	
1		$-\text{CH}=\text{CH}-\text{CH}=\text{CH}$		[194-196]
2	"	"		[207-208]
3	"	"		
4	"	"		
5	"	"		
6	"	"		

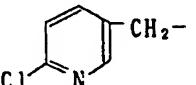
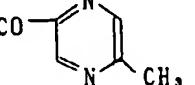
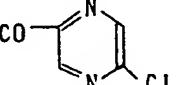
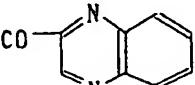
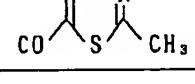
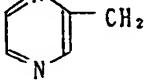
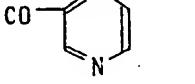
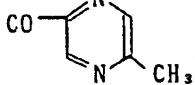
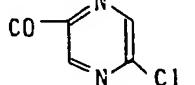
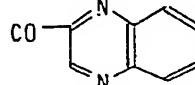
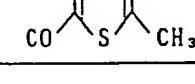
to be continued

5	7	CH <sub>2</sub> -	-CH=CH-CH=CH		
10	8	"	"		[220 up]
15	9	"	"		
20					[148 - 150]
25	10	"	"		
30	11	"	"		
35	12	"	"		
40	13	"	"		
45	14	"	"		
50	15	"	"		[158 - 159]
	16	"	"		

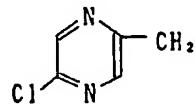
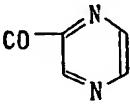
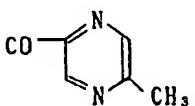
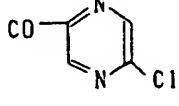
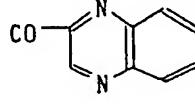
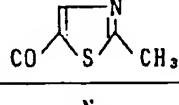
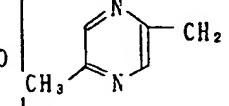
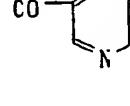
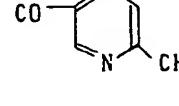
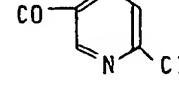
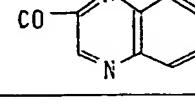
to be continued

5	17		-CH=CH-CH=CH		
10	18	"	"		
15	19	"	"		
20	20	"	"		$n_{D}^{26}$ 1.6085
25	21	"	"		
30	22	"	"		[218-220]
35	23	"	"		[172-173]
40	24	"	"		[151-153]
45	25	"	"		
50					

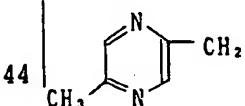
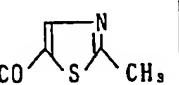
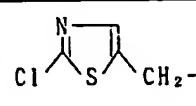
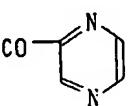
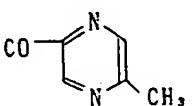
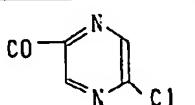
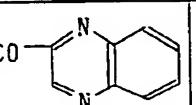
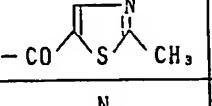
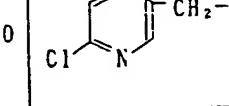
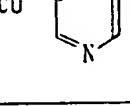
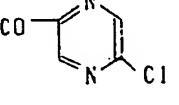
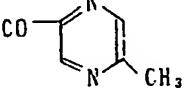
to be continued

5	26		-CH=CH-CH=CH		
10	27	"	"		
15	28	"	"		
20	29	"	"		
25	30		"		
30	31	"	"		
35	32	"	"		
40	33	"	"		
45	34	"	"		
50					

to be continued

5	35		-CH=CH-CH=CH		
10	36	"	"		
15	37	"	"		
20	38	"	"		
25	39	"	"		
30	40		"		[185 - 188]
35	41	"	"		
40	42	"	"		
45	43	"	"		
50					

to be continued

5	44 	-CH=CH-CH=CH		
10	45 	"		[173 - 175 dec]
15	46 "	"		
20	47 "	"		
25	48 "	"		
30	49 "	"		
35	50 	-CH=CH-CH=CH		
40	51 "	"		
45	52 "	"		
50				

to be continued

5	53		$-\text{CH}_3$ $-\text{CH}=\text{C}-\text{CH}=\text{CH}$	
10	54	"	"	
15	55	"	"	
20	56	"	"	
25	57	"	"	
30	58	"	"	
35	59	"	"	
40	60		$-\text{CH}=\text{CH}-\text{S}$	$-\text{CHO}$
45	61	"	"	$\text{COCH}_3$
50	62	"	"	$\text{COCH}_2\text{OCH}_3$
	63	"	"	$\text{COCH}_2\text{Cl}$

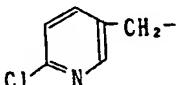
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5				
10	64	CH <sub>2</sub> -	-CH=CH-S	CO C <sub>2</sub> H <sub>5</sub>
15	65	"	"	COCH<sup>CH</sup> <sub>3</sub>
20	66	"	"	CO C <sub>3</sub> H <sub>7</sub> (n)
25	67	"	"	COCH=CH <sub>2</sub>
30	68	"	"	CO-
35	69	"	"	CO-
40	70	"	"	CO-
45	71	"	"	CO-
50	72	"	"	CO-
	73	"	"	CO-

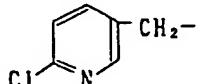
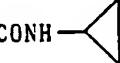
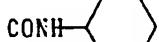
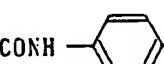
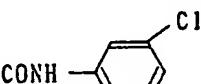
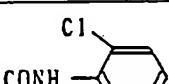
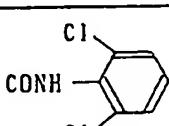
to be continued

5	74		- CH=CH-S		
10	75	"	"		
15	76	"	"		
20	77	"	"		
25	78	"	"		
30	79	"	"		
35	80	"	"		
40	81	"	"		
45	82	"	"		
50	83	"	"		[167-168]

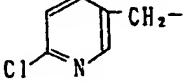
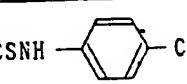
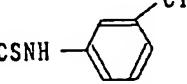
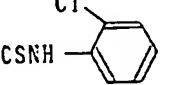
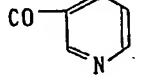
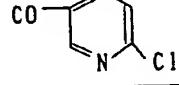
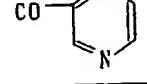
to be continued

5	84		- CH=CH-S	SO <sub>2</sub> CH <sub>2</sub> Cl	
10	85	"	"	SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	
15	86	"	"	SO <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	
20	87	"	"	SO <sub>2</sub> N<sup>CH <sub>3</sub> </sup><sub>CH <sub>3</sub> </sub>	
25	88	"	"	SO <sub>2</sub> CF <sub>3</sub>	
30	89	"	"	SO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -CH <sub>3</sub>	
35	90	"	"	SO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -Cl	
40	91	"	"	SO <sub>2</sub> -C <sub>12</sub> H <sub>9</sub>	
45	92	"	"	SO <sub>2</sub> -C <sub>12</sub> H <sub>9</sub>	
50	93	"	"	CONHCH <sub>3</sub>	(95-97)

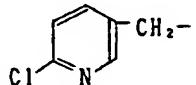
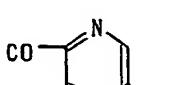
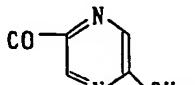
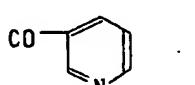
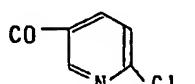
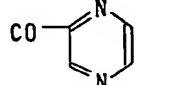
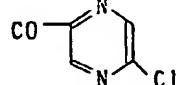
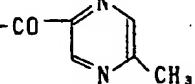
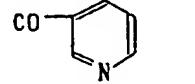
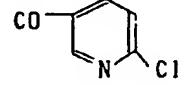
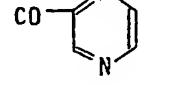
to be continued

5	94		-CH=CH-S	CONHC <sub>2</sub> H <sub>5</sub>	
10	95	"	"	CONHCH <sub>2</sub> CH=CH <sub>2</sub>	
15	96	"	"	CONHC <sub>4</sub> H <sub>9</sub> (t)	
20	97	"	"	CONH 	
25	98	"	"	CONH 	
30	99	"	"	CONH  [153 - 154]	
35	100	"	"	CONH 	
40	101	"	"	CONH 	
45	102	"	"	CONH 	[70 - 71]
50	103	"	"	CSNHCH <sub>3</sub>	

to be continued

5	104		-CH=CH-S	CSNH <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	
10	105	"	"	CSNHCH <sub>2</sub> CH=CH <sub>2</sub>	
15	106	"	"	CSNH- 	
20	107	"	"	CSNH- 	
25	108	"	"	CSNH- 	
30	109	"	"	CSNHCOOC <sub>2</sub> H <sub>5</sub>	
35	110	"	"	COOC <sub>2</sub> H <sub>5</sub>	
40	111	"	$\begin{matrix} \text{CH}_3 \\   \\ -\text{C}=\text{CH}-\text{S} \end{matrix}$		
45	112	"	"		
50	113	"	"		(153- 156dec)

to be continued

5	114		$\begin{matrix} \text{CH}_3 \\   \\ -\text{C}=\text{CH}-\text{S} \end{matrix}$		
10	115	"	"		(185- 188dec)
15	116	"	$\begin{matrix} \text{CH}_3 & \text{CH}_3 \\   &   \\ -\text{C}=\text{C}-\text{S} \end{matrix}$		...
20	117	"	"		
25	118	"	"		(193- 195dec)
30	119	"	"		
35	120	"	"		
40	121	"	$\begin{matrix} \text{CH}_3 \\   \\ -\text{CH}=\text{C}-\text{S} \end{matrix}$		
45	122	"	"		
50	123	"	"		[210°C up]

to be continued

5	124				
10	125	"	"		
15	126	"			
20	127	"	"		
25	128	"	"		
30	129	"	"		
35	130	"	"		
40	131	"			[151-153]
45	132	"	"		
50					

to be continued

5	133		-CH=CH-S		[164-165]
10	134	"	"		[157-158]
15	135	"	"		
20	136	"	"		
25	137	"	"		
30	138	"	"		
35	139	"	"		
40	140	"	"		
45	141	"	"		
50	142	"	"		

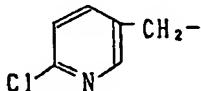
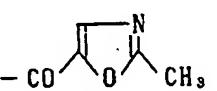
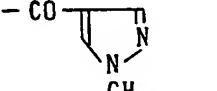
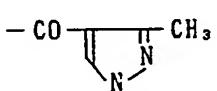
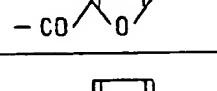
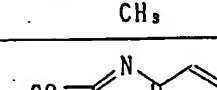
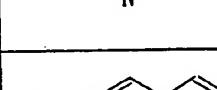
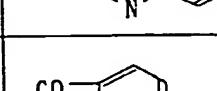
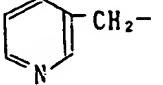
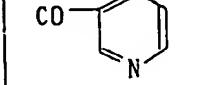
to be continued

5	143		-CH=CH-S-		
10	144	"	"		
15	145	"	"		[220° up]
20	146	"	"		[186-187]
25	147	"	"		
30	148	"	"		
35	149	"	"		
40	150	"	"		
45	151	"	"		
50					

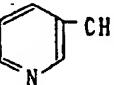
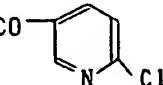
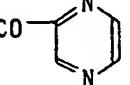
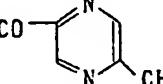
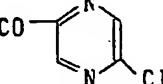
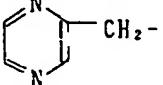
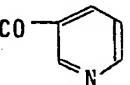
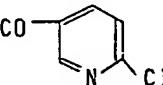
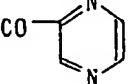
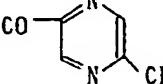
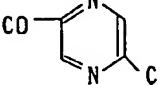
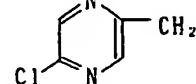
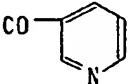
to be continued

5	152		- CH=CH-S		[205 - 206]
10	153	"	"		
15	154	"	"		
20	155	"	"		
25	156	"	"		
30	157	"	"		
35	158	"	"		
40	159	"	"		
45	160	"	"		[181 - 183]
50	161	"	"		
	162	"	"		

to be continued

5	163		-CH=CH-S		
10	164	"	"		
15	165	"	"		
20	166	"	"		
25	167	"	"		
30	168	"	"		
35	169	"	"		
40	170	"	"		
45	171		"		
50					

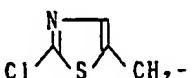
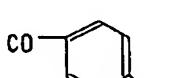
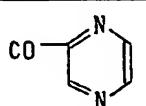
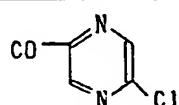
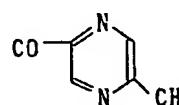
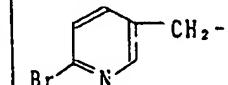
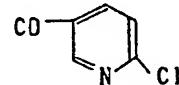
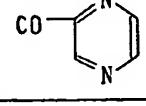
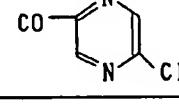
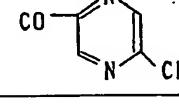
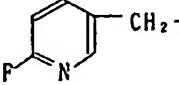
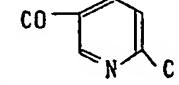
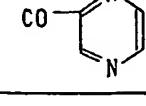
to be continued

5	172		-CH=CH-S-		
10	173	"	"		
15	174	"	"		
20	175	"	"		
25	176		"		
30	177	"	"		
35	178	"	"		
40	179	"	"		
45	180	"	"		
50	181		"		

to be continued

5	182	-CH=CH-S		
10	183	"	"	
15	184	"	"	
20	185	"	"	
25	186	"	"	
30	187	"	"	
35	188	"	"	
40	189	"	"	
45	190	"	"	
50	191	"	"	

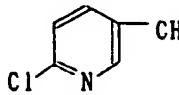
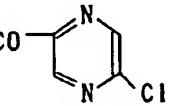
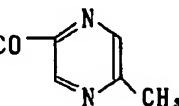
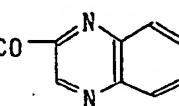
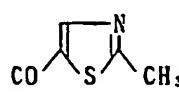
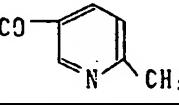
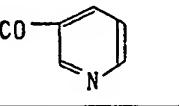
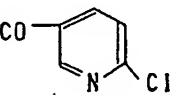
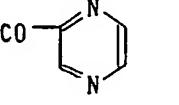
to be continued

5	192		-CH=CH-S-		
10	193	"	"		[155- 157dec]
15	194	"	"		
20	195	"	"		
25	196		"		
30	197	"	"		
35	198	"	"		
40	199	"	"		
45	200		"		
50	201	"	"		

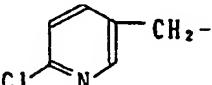
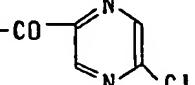
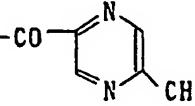
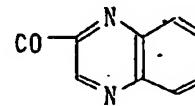
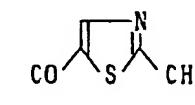
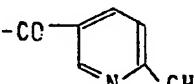
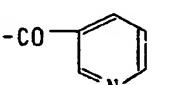
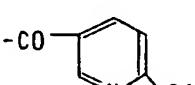
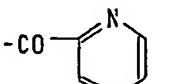
to be continued

5	202	-CH <sub>2</sub> -	-CH=CH-S		
10	203	"	"		
15	204	-CH <sub>2</sub> -	"		
20	205	"	"		
25	206	"	"		
30	207	"	"		
35	208	-CH <sub>2</sub> -	-CH=CH-CH <sub>2</sub>		
40	209	"	"		
45	210	"	"		
50	211	"	"		

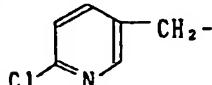
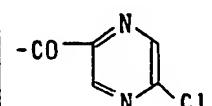
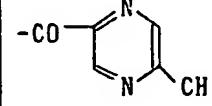
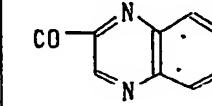
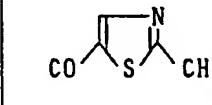
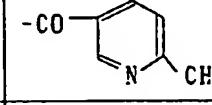
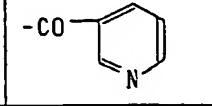
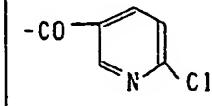
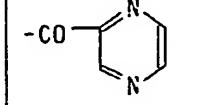
to be continued

5	212		$-\text{CH}=\text{CH}-\text{CH}_2-$		
10	213	"	"		
15	214	"	"		
20	215	"	"		
25	216	"	"	$\text{CSNHCOOC}_2\text{H}_5$	
30	217	"	"	$\text{SO}_2\text{CH}_3$	
35	218	"	$-\text{CH}=\text{CH}-\text{NH}$		
40	219	"	"		
45	220	"	"		
50	221	"	"		

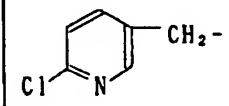
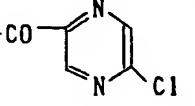
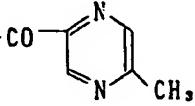
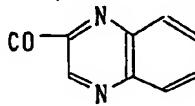
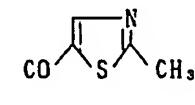
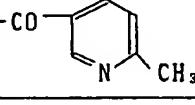
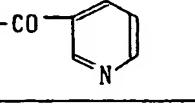
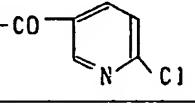
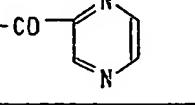
to be continued

5	222		-CH=CH-NH		
10	223	"	"		
15	224	"	"		
20	225	"	"		
25	226	"	"	CSNHCOOC <sub>2</sub> H <sub>5</sub>	
30	227	"	"	SO <sub>2</sub> CH <sub>3</sub>	
35	228	"	-CH=CH-CH=N		
40	229	"	"		
45	230	"	"		
50	231	"	"		

to be continued

5	232		-CH=CH-CH=N		
10	233	"	"		
15	234	"	"		
20	235	"	"		
25	236	"	"	CSNHCOOC <sub>2</sub> H <sub>5</sub>	
30	237	"	"	SO <sub>2</sub> CH <sub>3</sub>	
35	238	"	-CH=CH-CH <sub>2</sub> -S		
40	239	"	"		
45	240	"	"		
50	241	"	"		

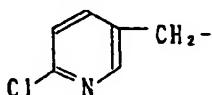
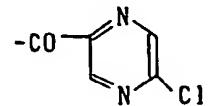
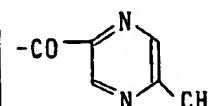
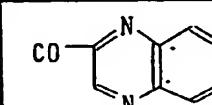
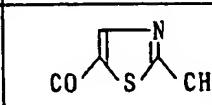
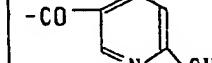
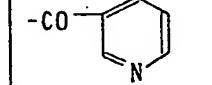
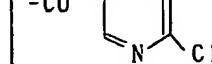
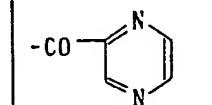
to be continued

5	242		-CH=CH-CH <sub>2</sub> -S		
10	243	"	"		
15	244	"	"		
20	245	"	"		
25	246	"	"	CSNHCOOC <sub>2</sub> H <sub>5</sub>	
30	247	"	"	SO <sub>2</sub> CH <sub>3</sub>	
35	248	"	-CH=CH-CH <sub>2</sub> -O		
40	249	"	"		
45	250	"	"		
50	251	"	"		

to be continued

5	252		-CH=CH-CH <sub>2</sub> -O		
10	253	"	"		
15	254	"	"		
20	255	"	"		
25	256	"	"	CSNHCOOC <sub>2</sub> H <sub>5</sub>	
30	257	"	"	SO <sub>2</sub> CH <sub>3</sub>	
35	258	"	-CH=CHO		
40	259	"	"		
45	260	"	"		
50	261	"	"		

to be continued

5	262		-CH=CHO		
10	263	"	"		
15	264	"	"		
20	265	"	"		
25	266	"	"	CSNHCOOC <sub>2</sub> H <sub>5</sub>	
30	267	"	"	SO <sub>2</sub> CH <sub>3</sub>	
35	268	"	-CH=CH-S		
40	269	"	"		
45	270	"	"		
50	271	"	"		[163-165]

to be continued

5	272		-CH=CH-S		
10	273	"	"		
15	274	"	"		
20	275	"	"		
25	276	"	"	CSNHCOOC <sub>2</sub> H <sub>5</sub>	
30	277	"	"	SO <sub>2</sub> CH <sub>3</sub>	
35	278	"			
40	279	"	"		
45	280	"	"		
50	281	"	"		[109-111]

to be continued

5	282		$\text{C}_2\text{F}_3$ $\text{---N}=\text{C}(\text{---S})$		
10	283	"	"		
15	284	"	"		
20	285	"	"		
25	286	"	"	$\text{CSNHCOOC}_2\text{H}_5$	
30	287	"	"	$\text{SO}_2\text{CH}_3$	
35	288		"		[138-139]

40 An insecticide specified in the present invention contains a compound having the general formula [I] as  
 an active ingredient. Although this compound can be used without formulating, it is normally used in a  
 typical form for agricultural chemicals, i.e. wettable powder, water-soluble powder, dust, emulsifiable  
 concentrate, granules, flowable, smoke generator, fumigant and the like. For additives and carriers, when  
 using them for solid formulation, plant-origin powder such as soybean powder and wheat flour; mineral fine  
 45 powder such as diatomaceous earth, apatite, gypsum, talc, bentonite and clay; and organic and inorganic  
 compounds such as sodium benzoate, urea and Glauber's salt can be used.

For a liquid formulation, vegetable oil; mineral oil; distilled fractions of petroleum such as kerosene,  
 xylene and solvent naphtha; cyclohexane; cyclohexanone; dimethylformamide; dimethylsulfoxide; trichloroethylene;  
 50 methylisobutylketone; water and the like can be used as a solvent. In the formulations  
 described above, if necessary, a surfactant can be added thereto in order to give homogeneous and  
 stabilized dilution. The wettable powder, the emulsifiable concentrate, the water-soluble powder and the  
 flowable prepared as described above can be used after diluting to the prescribed concentrations of  
 suspension or emulsion in water, whereas the dust and the granules can be used directly without diluting by  
 means of spraying plant crops.

55 Although the compounds specified in the present invention are, of course, sufficiently effective even in  
 single use, they can be also used as the mixture with various insecticides, acaricides and fungicides.

Representative acaricides and insecticides which can be used as a mixture with the compound  
 specified in the present invention include the following.

## Acaricides (Fungicides):

5 Chorobenzylate, chloropropylate, proclonol, phenisobromolate, dicofol, dinobuton, binapacryl, chlorphenamidine, amitraz, BPPS, PPPS, benzomate, hexythiazox, tenbutatin oxide, polynactin, quinomethionate, thioquinox, CPCBS, tetradifon, kayicide, avermectin, chlofentezin, flubenzimin, flufenoxuron, BCPE, cyhexatin, pyridaben, fenproximate, fenezaquin, thiophanate methyl, benomyl, thiuram, IBP, EDDP, phthalide, probenazole, isoprothiolane, TPN, captan, polyoxin, blastcidin-S, kasugamycin, validamycin, tricyclazole, pyroquilon, phenazin oxide, mepronil, flutolanil, pencycuron, iprodione, hymexazol, metalaxyl, triflumizol, diclomezine, tecloftalam, vinclozolin, procymidone, bitertanol, triadimefon, prochloraz, pirifenox, fenarimol, 10 fenpropimorph, trifoline, oxycarboxin, pefrazeate, diclomezine, fluazinam, oxadixyl, ethoavinolac, TPTH, propamocarb, fosetyl, dihydrostreptomycin, anilazine, dithianon, diethofencarb;

## Organophosphorous and carbamate insecticides (acaricides):

15 Fenthion, fenitrothion, diazinon, chlorpyriphos, ESP, vamidothion, fentoate, dimethoate, formothion, malathion, dipteryx, thiometon, phosmet, menazon, dichlorvos, acephate, EPBP, diaryfol, methyl parathion, oxydimeton methyl, ethion, pyrachlofos, monocrotophos, aldicarb, propoxur, methomyl, BPMC, MTMC, NAC, cartap, carbosulfan, benfuracarb, pirimicarb, ethofencarb, fenoxy carb, thiodicarb, salithion, carbofuran, 20 methocarb;

20 Pyrethroid insecticides (acaricides):

25 Permethrin, cypermethrin, decamethrin, fenvalerate, fenpropathrin, pyrethrin, tetramethrin, resmethrin, dimethrin, propathrin, bifenthrin, prothrin, fivalinate, cyfluthrin, cyhalothrin, flucythrinate, ethofenprox, cycloprothrin, tralomethrin, silaneophene;

## Benzoylureas and other insecticides:

30 Diflubenzuron, chlorfluazuron, triflumuron, teflubenzuron, buprofezin, pyriproxyphen, and machine oil.  
The formulations comprising the compound of this invention are illustrated by the following Examples, however, a carrier and a surface active agent to be added to the formulation shall not be limited by the 35 following Examples.

Example 3: Emulsifiable concentrate

35

40

A compound of the invention	10 parts
Alkyl phenylpolyoxyethylene	5 parts
Dimethylformamide	50 parts
Xylene	35 parts

Above components are mixed and dissolved to obtain the formulation. Upon use, the formulation is diluted with water to give the emulsion thereof, then the emulsion is sprayed.

45

Example 4: Wettable powder

50

A compound of the invention	20 parts
Sulfate ester of higher alcohol	5 parts
Diatomaceous earth	70 parts
Artificial silicate	5 parts

55 Above components are mixed and micronized to obtain the formulation. Upon use, the formulation is diluted with water to give the suspension thereof, then the suspension is sprayed.

Example 5: Dust

5

A compound of the invention	5 parts
Talc	94.7 parts
Artificial silicate	0.3 parts

10 Above components are mixed and pulverized to obtain the formulation. Upon use, the formulation is applied directly without diluting.

Example 6: Granular formulation

15

20

A compound of the invention	5 parts
Clay	73 parts
Bentonite	20 parts
Sodium dioctylsulfosuccinate	1 part
Sodium phosphate	1 part

Above components are mixed and granulated to obtain the formulation. Upon use, the formulation is applied directly without diluting.

25 Industrial ApplicationTest Example 1: Insecticidal efficacy against cotton aphids

Cotton aphids were inoculated at the rate of 30-50 aphids per plot on 10 days old cucumber leaves planted in a pot with diameter of 10 cm by using a small brush. The aphids injured during the inoculation were removed one day later, then the solution of the compound adjusted to 125 ppm by the dilution of the emulsifiable concentrate prepared according to the Example 3 with water was sprayed. The aphids were placed in an incubator maintained at 25 °C and 65% R.H., then the number of the living aphids was counted after 7 days to determine the control ratio of aphids by comparison with an untreated plot. The results are summarized in Table 2.

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[Table 2]

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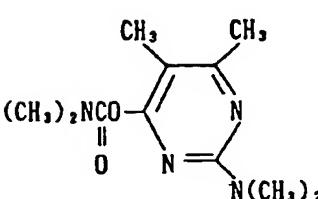
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50

55

Compound No.	Control Efficacy (7 days later) 125ppm (%)
1	100
2	100
8	100
9	100
15	100
20	100
22	100
23	100
40	100
45	100
83	100
93	100
113	100
115	100
118	100
123	100
131	100
133	100
134	100
145	100
146	100
152	100
160	100
271	100
Comparative Compound A	0
Comparative Compound B	100

## Comparative Compound A: Comparative Compound B:



(pyrimicarb)

(thiometon)

Test Example 2: Insecticidal efficacy against planthoppers

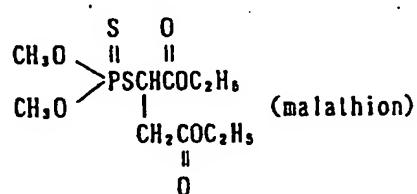
Young rice plant seedlings in a stage of 7 days after the germination were dipped for 30 seconds into a solution of the compound in water with a concentration of the compound of 125 ppm prepared by the 5 dilution of the emulsifiable concentrate prepared according to the protocol described in Example 3. After drying the seedlings were then put into a test tube and 10 third-instar larvae of a strain of planthoppers resistant against organophosphorous and carbamate insecticides were inoculated therein. The test tube was shielded with gauze and placed in an incubator maintained at 25°C and 65% R.H., and the mortality after 5 days was determined. The results were summarized in Table 3.

10

Table 3

15	Compound No.	Mortality (5 days later) 125ppm (%)
20	1	100
	2	100
	8	100
25	15	100
	20	100
	22	100
	24	100
30	40	100
	45	100
	83	100
	93	100
35	113	100
	115	100
	118	100
	123	100
	134	100
40	145	100
	146	100
	152	100
	160	100
	271	100
45	Comparative Compound C	0 0

## Comparative Compound C :



55 The compound specified in the present invention demonstrates excellent insecticidal activity on various species of pest insect such as the army worm, the diamondback moth, aphids, the green rice leafhopper and the brown rice planthopper. Recently, resistance to insecticides including organophosphorus and carbamate compounds has developed among various insect species such as the diamondback moth,

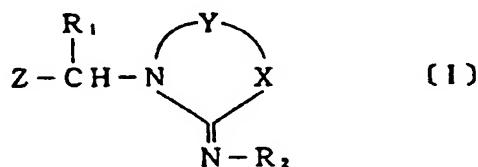
leafhopper, planthopper and aphids, resulting in a problem of insufficient efficacy of the insecticides described above against those insects. Therefore, an effective insecticide for those insecticide-resistant insect species are urgently required. The compounds specified in the present invention have excellent insecticidal efficacy not only against insecticide-sensitive pest insects but also against strains of pest insects resistant to insecticides comprising organophosphorus and carbamate compounds.

## Claims

1. A compounds having the general formula [I]:

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15



20

wherein

Z is an unsubstituted or substituted 5- or 6-membered heterocyclic group containing nitrogen;

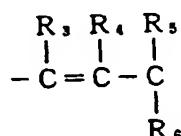
X is a carbon, nitrogen, sulfur or oxygen atom;

Y is, when X is a carbon atom, (a) in a form of -Y-X;

(a)

25

30



35

when X is a nitrogen atom, (b) or (c) in a form of -Y-X;

(b)

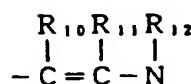
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(c)

45

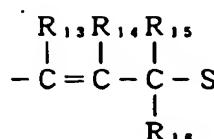


50

when X is a sulfur atom, (d), (e) or (f) in a form of -Y-X;

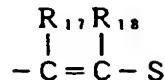
(d)

55



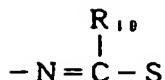
(e)

5



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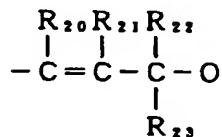
(f)



15

when X is an oxygen atom, (g) or (h) in a form of -Y-X;  
 (g)

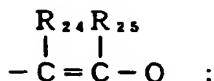
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(h)

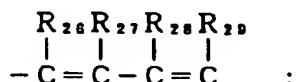
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$\text{R}_2$  is an electron attractive group other than nitro, cyano and trifluoroacetyl;  
 $\text{R}_1$  and  $\text{R}_3 \sim \text{R}_{25}$  are independently a hydrogen atom, a halogen atom or an unsubstituted or substituted lower alkyl;  
 Or, Y is, when X is a carbon atom, (i) in a form of -Y-X;  
 (i)

40



45

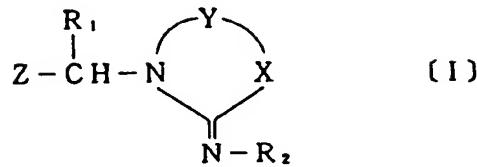
$\text{R}_2$  is an unsubstituted or substituted heterocyclic carbonyl, other than furancarbonyl, thiophenecarbonyl and pyridinecarbonyl;  
 $\text{R}_{26} \sim \text{R}_{29}$  are independently a hydrogen atom, a halogen atom or an unsubstituted or substituted lower alkyl;  
 or its salt.

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2. A process for preparing a compound represented by the general formula [I]:

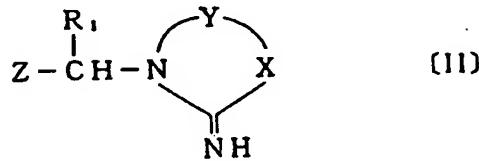
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10 wherein Z, X, Y, R<sub>1</sub> and R<sub>2</sub> are as defined above, characterized in that a compound represented by the general formula [II]:

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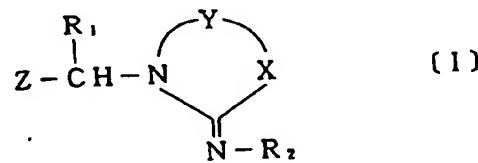


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wherein Z, R<sub>1</sub>, X and Y are as defined above, are reacted with a compound represented by the formula R<sub>2</sub>-Hal, wherein Hal and R<sub>2</sub> are as defined above.

25 3. An insecticide characterized in that the insecticide comprises one or two or more compounds represented by the general formula [I]:

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wherein Z, X, Y, R<sub>1</sub> and R<sub>2</sub> are as defined above, as effective ingredients.

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## INTERNATIONAL SEARCH REPORT

International Application No PCT/JP92/00283

### I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC  
 Int. Cl<sup>5</sup> C07D213/81, C07D401/06, C07D413/06, C07D413/14,  
 C07D417/06, C07D417/14, C07D401/14

### II. FIELDS SEARCHED

Minimum Documentation Searched †

Classification System	Classification Symbols
IPC	C07D213/81, C07D401/06, C07D401/14, C07D413/06, C07D413/14, C07D417/06, C07D417/14
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched †	

### III. DOCUMENTS CONSIDERED TO BE RELEVANT \*

Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages **	Relevant to Claim No. ‡
A	US, A, 3,622,585 (Parke, Davis and Co.), November 23, 1971 (23. 11. 71)	1-3

\* Special categories of cited documents: †

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "G" document member of the same patent family

### IV. CERTIFICATION

Date of the Actual Completion of the International Search <b>May 21, 1992 (21. 05. 92)</b>	Date of Mailing of this International Search Report <b>June 9, 1992 (09. 06. 92)</b>
International Searching Authority <b>Japanese Patent Office</b>	Signature of Authorized Officer

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